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A R M S T R O N G   L A B O R A T O R Y

AN EVALUATION OF THE TECHNICAL FEASIBILITY OF THE PACKED TOWER ADVANCED OXIDATION PROCESS FOR THE REMOVAL AND DESTRUCTION OF CONTAMINANTS FROM WATER

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This report has been reviewed and is approved for publication.

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14. Abstract   This final report describes the research work done to investigate the behavior of a packed column contactor as an ozonation reactor for destruction of organic contaminants in groundwater treatment. Both a laboratory and pilot-scale column have been used during experiments to gather scale up information for such a system. The columns have been operated in either cocurrent and counter current mode using trichloroethylene (TCE) at low ppm levels in water as the contaminant. The TCE removal and destruction has been measured as a function of gas to liquid (G/L) ratio, contacting pattern, and ozone concentration. Using the experimental results and literature information, mathematical modeling has been done to describe and simulate the system behavior.

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PREFACE

This final report describes the research work done to investigate the behavior of a packed column contactor as an ozonation reactor for destruction of organic contaminants in groundwater treatment. Both a laboratory and pilot-scale column have been used during experiments to gather scale up information for such a system. The columns have been operated in either cocurrent and counter current mode using trichloroethylene (TCE) at low ppm levels in water as the contaminant. The TCE removal and destruction have been measured as a function of gas to liquid (G/L) ratio, contacting pattern, and ozone concentration. Using the experimental results and literature information, mathematical modeling has been done to describe and simulate the system behavior.

EXECUTIVE SUMMARY

A. OBJECTIVE

The purpose of this portion of the research was to investigate the behavior of a packed-column contactor as an ozonation reactor for groundwater treatment. The effect of contacting patterns, concentration, flowrates, and gas to liquid ratios are examined. A mathematical model for performance evaluation and prediction is also developed.

B. BACKGROUND

Contamination of ground water is a common environmental problem. A frequent contaminant is the presence of chlorinated hydrocarbons (CHC) originating from the spill of cleaning fluids or solvents. In recent years contaminants of this type have been removed by air stripping of the affected water. Although air stripping is a very effective measure to remove CHC with their high vapor pressure, it creates a second problem by producing a contaminated off gas. Simple discharge of the exhaust gas into the atmosphere is no longer acceptable. A promising process avoiding this problem is wet oxidation of the contaminants using ozone as the oxidizing agent. The result of such an ozonation process is the decomposition of CHC into harmless substances such as carbon dioxide, water, and inorganic salts.

C. SCOPE

The behavior of a packed-column contactor as an ozonation reactor for water treatment has been investigated using both a laboratory- and pilot-scale column. The columns have been operated in either cocurrent and counter current mode using trichloroethylene (TCE) at low ppm levels in water as the contaminant. The TCE removal and destruction have been measured as function of gas-to-liquid (G/L) ratio, contacting pattern, and ozone concentration. The mass transfer coefficient for TCE stripping has been determined from air-stripping studies, and the mass transfer coefficient for ozone absorption determined from indigo dye reaction experiments. The specific ozone utilization rate for different waters, including a ground water sample from K. I. Sawyer AFB, to be treated has also been determined. From this information, a multiphase plug flow reactor model has been developed to predict the removal of trichloroethylene (TCE) from water in an up-flow co-current packed bubble column. The model consists of material balances on both the gas and liquid phase TCE and ozone as functions of column length or contact time. By using the mass transfer parameters and fitting the intrinsic reaction rate constant for TCE and ozone to experimental data, a computer program for predictions of scaled-up reactor performance has been created. A batch test on the raw water to be treated, determining the specific ozone utilization rate, is all that is necessary to provide a rough performance prediction. Trials with this model indicate that a set of reactors in series with parallel ozone feeds produces the highest removal efficiency for TCE, and that limited ozone holdup may be the limiting design factor with regards to column height. A sensitivity analysis also indicates that the gas/liquid ratio and ozone

concentration have the greatest effect on reactor performance.

D. RESULTS

The removal and destruction of TCE were determined for both the bench-scale and pilot-scale columns over a range of G/L ratios, ozone concentrations, contacting patterns, and contact times. This range of parameters produces a wide variety of information on the removal efficiencies and destruction rates. For countercurrent operation, the experimental data show a strong influence of G/L ratio on TCE stripping with up to 70 % being stripped at a G/L ratio of two. When using low G/L ratios of one or below, the ozone feed gas concentration becomes important. A maximum in TCE removal is reached here at a concentration of 17 mg/l. Similar experiments for cocurrent and countercurrent operation indicate less volatiliazation and higher TCE destruction for cocurrent mode. Finally the liquid and gas phase concentration profiles sudgest a liquid residence time of about one to two minutes and a gas residence time of no more than 30 to 40 seconds.

E. CONCLUSIONS AND RECOMMENDATIONS

A bench- and pilot-scale packed-bubble column ozonation reactor has been developed and tested for a variety of flowrates, ozone concentrations, and contacting patterns. A plug flow model has been developed for the cocurrent flow case. The adjustable parameters for this model have been determined from literature sources and from fitting to the results of experimental data. The model in turn was then used to study several design options and operating conditions. Some of the major findings of this study include:

♦ A packed-bubble column (PBC) is at least an order of magnitude smaller than a comparable open-bubble column.

♦ A countercurrent flow pattern demonstrated a high degree of TCE stripping, and relatively low oxidation. A cocurrent upflow column demonstrated the lowest volatilization and highest oxidation of TCE. The contacting pattern selected depends on the relative volatility and reactivity of the contaminants.

♦ To minimize TCE volatilization and optimize TCE oxidation, low G/L ratios and high ozone concentrations should be employed.

♦ For the reaction with TCE in pure water, a reactor contact time of approximately 2 minute for the water, and 1 minute for the ozone approaches the greatest destruction for the minimum volume.

♦ By determining the specific ozone utilization rate, w, for "real" groundwater, the model may then be used to determine the appropriate reactor contact times to obtain a given degree of destruction. (By varying flowrates, or ozone dosage.)

♦ The models predict that the most efficient way of achieving high TCE destruction is to run the water phase through at least two reactors in series, and divide the ozone between the reactors in parallel.

♦ Actual groundwater may require high ozone dosages to achieve a high conversion. Proper water pretreatment to remove ozone depleting substances is essential for efficient reactor operation.

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SECTION I

INTRODUCTION

A. OBJECTIVE

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B. BACKGROUND

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SECTION II

THEORY

A. REACTIONS OF OZONE IN AQUEOUS SOLUTION

Ozone has been used as an aqueous oxidizing agent for over 80 years. Due to its high oxidation potential it has the ability in theory to completely mineralize a wide range of hydrocarbons and halogenated organics. The direct reaction between the compounds and ozone is actually very slow (Hoigne and Bader, 1); however, in water ozone may decompose to produce hydroxyl radicals which may react very rapidly with the same organics. Table 1 shows rate constants reported by Glaze (2) for several organic compounds. Glaze also reports that ozone reacts best in water as an electron acceptor (for the oxidation of metallic ions), as an electrophile (for the oxidation of phenol and other aromatics), and as a dipole addition agent (in carbon-carbon bonds). A generalized reaction model for the ozonolysis of organics in water is shown in Figure 1 (Staehelin and Hoigne, 3).

$$O_3 + R_i \longrightarrow \begin{cases} \text{Products} \\ OH^* + \text{Products} \end{cases}$$

$$O_3 + OH^- \longrightarrow [O_2^*]^- + HO_2^*$$

$$HO_2^* \rightleftharpoons H^+ + [O_2^-]^*$$

$$O_3 + O_2^{*-} + H_2O \longrightarrow OH^* + OH^- + 2O_2$$

$$O_3 + OH^* \longrightarrow HO_2^* + O_2$$

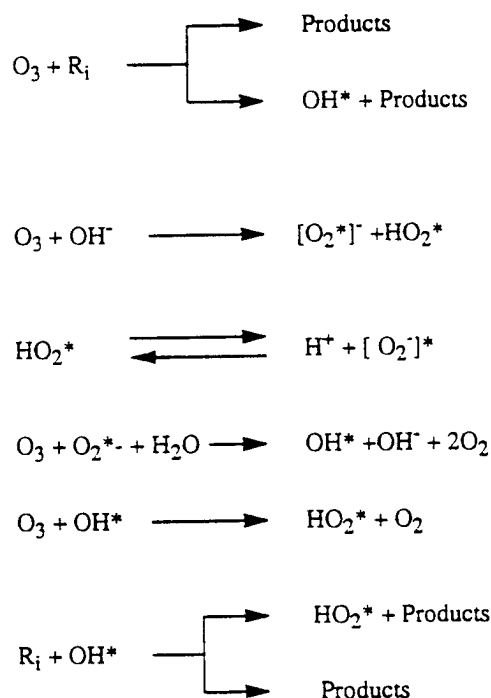$$R_i + OH^* \longrightarrow \begin{cases} HO_2^* + \text{Products} \\ \text{Products} \end{cases}$$

Figure 1. Proposed Reaction Scheme for Ozone with Organic Compounds in Aqueous Solution. (Staeheline ans Haigne, 1982 and 1985)

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Table 1: Relative reactivity of ozone and hydroxyl radicals.

Compound	Ozone $(M^{-1}s^{-1})$	Hydroxyl Radical $(M^{-1}s^{-1})$
Benzene	2	6×10^9
Cholrobenzene	0.8	6×10^9
Methanol	0.02	0.9×10^9
Carbonate ion	-	0.9×10^9
TCE (Trichloroethylene)	15	4.2×10^9
Indigo dye	10^7	(not available)

Ozone is consumed in three distinct ways, : (1) direct reaction of the ozone with the organic compound, R_i; (2) self-decomposition initiated by hydroxide ions, UV light, or various free radicals; or (3) production of hydroxyl radicals.

In groundwater, waste water, and other nonideal situations several factors may alter ozone's effectiveness. The presence of radical scavenging species, such as bicarbonates, reduces the efficiency of ozonolysis. Other species in solution (such as Fe^{+2}) may act as initiators and produce hydroxyl radicals in the presence of ozone in water. UV light also strongly interacts with dissolved ozone to produce hydroxyl radicals. Since these species serve to both quickly destroy the contaminants of concern, yet at the same time decompose the ozone itself, a delicate tradeoff exists between these two rates. The balance between these two processes may be described most simply by two rate parameters: (1) the specific reaction rate for the organic and ozone (or its reactive products in water), k_1; and (2) the specific ozone utilization rate , w, which quantifies the rate of consumption of ozone via all the reaction pathways including self-decomposition. The first parameter, k_1, is usually taken as a second order reaction rate constant; and the specific ozone utilization rate, w, is a pseudo-first order rate constant with respect to the ozone concentration. The methodology for determining w is to follow the decomposition of ozone for the water sample of concern in a batch reactor system. Yuteri (4) has attempted to quantify w (hr⁻¹) to account for the effect of pH, alkalinity ($CaCO_3$, mg/l), and total organic carbon (TOC, mg/l). His empirically derived equation is:

$$\log w = -3.98 + 0.66 pH + 0.61 \log(TOC) - 0.42 \log(alkalinity/10) \tag{1}$$

Ikemizu (5) and others have developed expressions for the self decomposition reaction of ozone which incorporate both the effects of hydroxide ion concentration and UV light intensity.

$$-\frac{dO_3}{dt} = k_a [OH^-]^{(0.28)} [O_3]^{(1.5)} + k_b [OH^-] [O_3] + k'I \cdot [OH^-]^{(0.07)} [O_3] \tag{2}$$

where k_a, k_b, and k' are recombination rate constants, and I is the light intensity in watts per square meter. However, in modelling a practical reactor it is unrealistic to incorporate a detailed mechanistic approach for the chemical kinetics, but instead one should use these two rather broad descriptors on a specific "water-by-water" basis, with the k_1 and w values determined experimentally when possible.

B OZONATION REACTOR CONFIGURATION

The rate constants discussed above remain virtually unchanged regardless of the reactor configuration. However, the reactor design has a tremendous effect on the overall performance of an ozonation unit due to the mass transfer coefficients for the reactants, and the degree of mixing (dispersion) within the reactor unit. This last factor is of particularly great importance since it largely determines the size and basic design of the reactor. Levenspiel (6) along with a great number of others has shown that for any positive order reaction, an "unmixed" plug flow reactor (PFR) is much smaller than its well-mixed counterpart (CSTR) for a given desired conversion. If one desires a high conversion (>99%) or has a higher reaction order (2nd or 3rd) the difference is particularly pronounced. So if one desires, for example, 99.9% destruction of an organic in water and we assume the reaction of ozone with the organic to be only first order (a second order assumption makes the difference greater) a homogeneous well mixed reactor would require a volume of 2178 ft^3 versus a PFR volume of 15 ft^3 to accomplish the same reaction. In light of this difference it is surprising that virtually all ozonation reactors are of the countercurrent, open bubble-column type, which more closely resembles a well-mixed reactor. Marinas (7) has shown that the degree of mixedness of such reactors is a strong function of the gas/liquid volumetric flowrate ratios (G/L). For G/L ratios greater than 0.1, open columns exhibited well-mixed behavior. On the other hand those authors showed that packed co-current ozonation columns exhibited PFR behavior over the entire range of their investigation. Without question, a packed co-current flow bubble column offers great advantages in terms of ozonation reactor size.

The reactor type used also greatly affects the rate of mass transfer for each of the reactants (ozone and organic) in a two phase (gas-liquid) reactor. Previous research with batch reactors (Baillod, 8; Glaze and Kang, 9; Bellamy, et. al, 10), open bubble columns (Aieta, 11; Khan, 12; Venosa, 13), and recirculating reactors (Sundstrom, 14) have shown that the rate of ozone mass transfer plays an important role, especially for reactive contaminants. When the liquid phase in a packed column is the continuous phase, it is termed a packed bubble column (PBC). The packing in a packed bubble column distributes the bubbles, creates thin films near the packing surfaces, and increases bubble residence time; thereby increasing the rate of mass transfer for ozone from the gas phase into the liquid phase as compared to bubble columns. Charpentier (15) states that the packed bubble column shows a 15 to 100% improvement in mass transfer compared to the unpacked columns. Vigorous agitation of bubble columns with impellers can provide comparable mass transfer, but obviously entailed the disadvantages of a well-mixed reactor and high power consumption.

A PBC's mass transfer performance is affected by the G/L ratios and ozone concentration. According to film theory, the processes involved in the mass transfer across gas-liquid boundary include: 1. diffusion of ozone from the gas phase to the interface; 2. equilibrium distribution of ozone between the gas and liquid at the interface (Henry's law behavior); and 3. diffusion of the

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ozone from the interface to the bulk liquid phase. Similarly, if the organic present in the liquid is volatile, the same set of steps will exist in reverse for the organic stripping out into the gas phase. Typically, steps 2 and 3 are fast and may be neglected, leaving a simple expression for the flux of component i, N_i (moles/s), from the gas to the liquid:

$$N_i = K_{1_i} A (C_i^* - C_i^{liquid})$$ (3)

where K_{1_i} is the mass transfer coefficient for component i, A is the gas-liquid interfacial area and the * superscript indicates an equilibrium concentration at the interface. This concentration is defined by Henry's law constant (dimensionless), H, where:

$$H_i = \frac{C_i^{gas}}{C_i^*}$$ (4)

The mass transfer coefficient is a strong function of reactor type, contacting pattern, and operating parameters such as flowrates. For many types of reactors, empirical correlations have been developed relating the operational parameters to the $K_1 A$. Several correlations have been suggested for multiphase reactors operating in the trickle bed regime (Satterfield, 16) where the continuous phase is the gas phase; however, we have not found any such general correlations for upflow PBCs. This leaves only experimental methods for determining the mass transfer characteristics of such devices.

One of the more commonly used methods of determining gas to liquid mass transfer coefficients is the use of the "instantaneous" reaction method (Charpentier, 15). The theory states that if the reaction occurring in the liquid phase is sufficiently fast, the overall rate will be determined by the rate of gas-to-liquid mass transfer. The decoloration of indigo dye with ozone is such a reaction. The color change is easy to follow via a visible light spectrometer, and the reaction stoichiometry is 1:1. Using this technique to determine the mass transfer coefficients for a PBC with 3/8 inch glass Raschig rings over a range of concentrations and flow conditions, Gupta (17) has proposed a simple mass transfer correlation of the form:

$$K_1 A = \beta (G/L)^\alpha$$ (5)

where the empirically fit constants are: $\alpha = -0.43$ and $\beta = 155$; $K_1 A$ has the units hr^{-1}, and G/L is the volumetric gas-to-liquid ratio.

C. MASS TRANSFER WITH REACTION IN OZONATION PROCESSES

A complete model for the kinetics of an PBC ozonation reactor includes both the rates of mass transfer and the specific reaction rates. Mass transfer across a phase boundary with reaction is extensively discussed in previous work (Danckwerts, 18; Levenspiel, 6; Charpentier, 15). Figure 2 represents the concentration profiles across a phase boundary for each reactant as envisioned by film theory. A series of steps is involved: (1) diffusion of the ozone from the

interface to the aqueous phase reaction zone; (2) diffusion of the organic, R_i, from the bulk liquid to the reaction zone; and (3) reaction in the aqueous phase between ozone and the organic, R_i. As in any process involving a number of steps in series, the rate is governed by the slowest step (Levenspiel, 6). If the chemical reaction is extremely rapid (essentially instantaneous), the process is almost entirely mass transfer limited. This case is useful in determining the mass transfer coefficients of a particular reactor configuration from experimental measurements (Gupta, 17). In the other extreme, when the reaction is very slow, mass transfer is unimportant, and equilibrium concentrations of the reactants are obtained in each phase. For moderately fast reactions (as with ozone and TCE), all three steps are important in analyzing reactor performance.

SECTION III

REACTOR MODELLING

This effort is intended to develop a process model for a packed column ozonation process in which moderate concentrations of ozone are used to oxidize dilute organic contaminants (e.g.-TCE) in groundwater. Although the model may not give precise effluent concentrations it is intended to provide guidance in the design, construction, and operation of a pilot scale unit.

For a moderately fast reaction (such as ozone-TCE) where the concentration of the gas phase ozone is held fairly constant, a mass transfer with first order reaction might be used. This assumption would hold true for relatively large amounts of ozone compared to that required for the stoichiometric destruction of the contaminant (a large excess of ozone). Although this assumption may not be valid for the operating conditions for the current experiments, this model has an analytical solution, allowing some qualitative assessment of the best mode of reactor flows and operation. This model requires accurate rate constants, k_1 (from experiments and literature), and liquid side mass transfer coefficients, K_1A. Charpentier (15) suggests a k_1 of .15/sec in a packed bubble column as an average value. For A he suggests the square root of the gas superficial velocity be used. The equations for this case have been implemented as MathCAD programs for solutions of the analytical expressions of removal as a function of bed height and contact time. We have tested this model for both the countercurrent mode and co-current flow modes using an arbitrary data set. For $K_1A \gg k_1$ the co-current mode appears better, and for $k_1 \gg K_1A$ the counter-current mode is more efficient in terms of contaminant destruction. If we accept the Charpentier figure for K_1A and a high value of k_1 for TCE the co-current mode is better.

A model for a cocurrent plug flow reactor with second order reactions has also been developed based upon that of Gurol (19). This model explicitly takes into account the ozone utilization efficiency by implementing the specific ozone utilization rate, w. This parameter combines the multiplicity of processes which consume zone in the reactor. The intrinsic reaction rate is only used for the rate of TCE disappearance. The other major change in this model is a second-order intrinsic oxidation model.

Gas Liquid Interface

Gas phase

Ozone →

Bulk Liquid Phase

R_i

Liquid Film

Concentration Profiles

$C_{R_i, bulk, liquid}$

$C_{O_3, bulk, gas}$
p

pi

$C_{R_i, bulk, gas}$

$C_{O_3, i}$

C_{R_i}

$C_{O_3, bulk, liquid}$
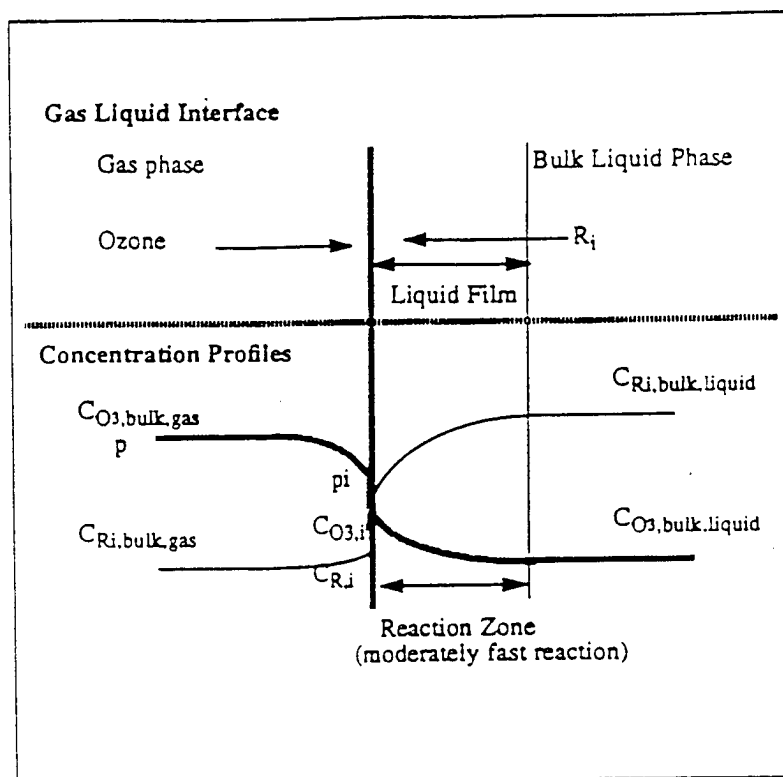
Reaction Zone
(moderately fast reaction)

Figure 2. Schematic of Concentration Profiles for Transfer of Ozone to Water and Consequent Reaction with an Organic in Solution.

The model consists of four differential material balances over a section of a PFR : ozone in the gas phase, ozone in the water phase, TCE in gas, and TCE in water. These may be expressed in differential form as a set of ordinary differential equations (ODE's), showing the ozone concentration, O_3 (gmol/liter), and TCE concentration, TCE (gmol/liter) over a volume element of the column. In order to make the design equations as flexible as possible for reactor scaleup, they are written in terms of reactor contact time, t. This contact time is directly linked to the column height, z, via the cross sectional area of the column, A, and the liquid volumetric flowrate, Q_L:

$$t = z \cdot \frac{A}{Q_l} \tag{6}$$

Gas-Phase O_3 is removed via absorption into the water.

$$\frac{dO_{3_g}}{dt} = K_1^{O_3} A \left(O_{3_l} - O_{3_{equilibrium}} \right) \left(\frac{Q_l}{Q_g} \right) \tag{7}$$

Here, Q_g is the volumetric gas flowrate, and the equilibrium ozone concentration is defined by Henry's law:

$$H_{O_3} = \frac{O_{3_g}}{O_{3_{equilibrium}}} \tag{8}$$

Liquid-phase O_3 is added from the gas phase and removed via several reactions. These are expressed as the specific ozone utilization rate, w.

$$\frac{dO_{3_l}}{dt} = K_1^{O_3} A \left(O_{3_{equilibrium}} - O_{3_l} \right) - h_l w O_{3_l} \tag{9}$$

where h_l is the liquid holdup for a volume of liquid and gas within the column, V:

$$h_l = \frac{V_{liquid}}{\left(V_{liquid} + V_{gas} \right)} \tag{10}$$

Liquid-phase TCE is removed from the water via both stripping and reaction.

$$\frac{dTCE}{dt} = K_1^{TCE} A \left(TCE_{equilibrium} - TCE_l \right) - h_l k_1 \left(TCE_l \cdot O_{3_l} \right) \tag{11}$$

where the $TCE_{equilibrium}$ is defined by the Henry's law constant for TCE, H_{TCE}.

Gas-phase TCE is added by stripping from the water phase.

$$\frac{dTCE_g}{dt} = K_1^{TCE} A \left(TCE_l - TCE_{equilibrium} \right) \left(\frac{Q_l}{Q_g} \right) \tag{12}$$

This model also assumes ideal plug flow, local gas-liquid interface equilibrium (Henry's law behavior), and no gas phase reactions. These 4 equations are linked via the concentration terms and therefore must be solved simultaneously. The second order reaction terms preclude an

analytical solution, and therefore a numerical computer solution must be employed. (In this case using a fourth order Runge-Kutta method.) This simple plug flow model has shown great utility with regards to modelling the cocurrent reactor.

To solve the equations, a FORTRAN based program has been written to run on an IBM compatible PC. This program incorporates a fourth-order Runge-Kutta integration routine to solve the equations, along with a subroutine to automatically compute the derivatives of the constitutive equations. This program is interactive in that it requests the major input variables for the reactor process. These need to be determined outside of the program in a manner described below. Output is in the form of ASCII or spreadsheet compatible files, which may be imported to a graphing program for display of the results.

The countercurrent case has essentially the same mathematical form, but the signs for the equations for one of the phases are negative and the solution becomes a boundary value problem instead of an initial value problem.

Gas-phase O_3 is removed via absorption into the water.

$$\frac{dO_{3_g}}{dt} = K_1^{O_3} A \left(O_{3_l} - O_{3_{equilibrium}} \right) \left(\frac{Q_l}{Q_g} \right) \tag{13}$$

Here, Q_g is the volumetric gas flow rate, and the equilibrium ozone concentration is defined by Henry's law:

$$H_{O_3} = \frac{O_{3_l}}{O_{3_{equilibrium}}} \tag{14}$$

Liquid-phase O_3 is added from the gas phase and removed via several reactions. These are expressed as the specific ozone utilization rate, w.

$$-\frac{dO_{3_l}}{dt} = K_1^{O_3} A \left(O_{3_{equilibrium}} - O_{3_l} \right) - h_l w O_{3_l} \tag{15}$$

where h_l is the liquid holdup for a volume of liquid and gas within the column, V:

$$h_l = \frac{V_{liquid}}{\left(V_{liquid} + V_{gas} \right)} \tag{16}$$

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Liquid-phase TCE is removed from the water via both stripping and reaction.

$$-\frac{dTCE}{dt} = K_l^{TCE} A \left(TCE_{equilibrium} - TCE_l \right) - h_l k_1 \left(TCE_l \cdot O_{3_l} \right) \tag{17}$$

where the $TCE_{equilibrium}$ is defined by the Henry's law constant for TCE, H_{TCE}.

Gas-phase TCE is added by stripping from the water phase.

$$\frac{dTCE_g}{dt} = K_l^{TCE} A \left(TCE_l - TCE_{equilibrium} \right) \left(\frac{Q_l}{Q_g} \right) \tag{18}$$

SECTION IV

MODEL PARAMETER ESTIMATION

A major obstacle in solving these equations is determining the appropriate values for several of the constants. Some of these parameters are set by the design constraints and thus well known: 1. the liquid holdup, h_l. 2. the gas and liquid volumetric flowrates, Q_l and Q_g; 3. the Henry's Law constants for TCE and Ozone, H_{O3} and H_{TCE}; and the initial concentrations of TCE and ozone. Four other parameters are not well defined and must be extrapolated from other experiments or the open literature: the mass transfer coefficients for TCE and ozone, K_lA_{TCE} and K_lA_{Oz}; the specific ozone utilization rate, w; and the reaction rate between ozone and TCE (in the presence of UV), k_1. For the first 4 values we used a standard holdup figure for a PBC of ($h_l=0.91$); the flowrates anticipated for water and ozone respectively; the literature values for Henry's law constants are used ($H_{TCE} = 0.43$ mmHg/mol and $H_{O3} = 2.82$ mmHg/mol (Venosa, 13)); and finally, initial concentrations of 10 ppm by weight for TCE and the corresponding concentration for ozone.

The last four values (K_lA's, k, and w) are less straightforward without direct experimental values on the process and were estimated from other sources to test the model. These were obtained using the ozone-indigo dye experiment and the analytical scheme for instantaneous reaction described previously. This estimate should be accurate for the glass Raschig rings used as packing, since K_lA is relatively independent of concentration. For very low gas/liquid ratio values of K_lA for ozone of 0.026 to .058 sec^{-1} was found in our experiments. This value is close to that suggested by Gurol (19), but somewhat less than the value of 0.15 sec-1 suggested by Charpentier (15). Table 2 summarizes some of these values found experimentally. To be conservative in the calculations the lower range of values was used. As for the TCE mass transfer coefficient, Charpentier suggests as a rule that the K_l's are directly proportional to the diffusion coefficient, D, (this follows from Fick's law) leading to a conservative value of $K_lA = 0.02$ sec^{-1} for TCE. Via airstripping experiments on TCE we calculated relatively low values on the order of 0.004 sec-1, indicating that gas-liquid equilibrium might actually control the transfer process (See Table 2)

Table 2: EXPERIMENTALLY DETERMINED MASS TRANSFER COEFFICIENTS.

Volumetric G/L Ratio	0.5	1.0	2.0
Liquid Load (liter/min m^2)	KlA for TCE (1/s)	KlA for TCE (1/s)	KlA for TCE (1/s)
174.4	0.00056	0.00185	0.00198
290.7	0.00082		
523.26	0.00185	0.00452	
Vapor Load (liter/min m^2)	KlA for ozone (1/s)	KlA for ozone (1/s)	KlA for ozone (1/s)
261.6	0.026	0.043	0.058

The two reaction rate constants, w and k_1, are the most difficult to estimate, requiring direct experimental data. The specific ozone utilization rate includes both the reaction with TCE and ozone decomposition. We could have estimated the decomposition using the method of Ikemizu (5); but their equation requires accurate light and pH information and several other parameters that are poorly known for the reactors involved. So, the approach taken was to use the batch reaction data and calculate w. The range of values calculated for various water samples are shown in Table 3. These are close to other such rates in the literature. Finally, with regards to the TCE - ozone reaction rate constant, k_1, there is not much to go on. Most of the values in the literature are ambiguous (Hoigne, 1, Gurol, 19; See Table I). As a test case, we fit the model to the data from MTU to determine an initial value of k_1. After doing a one parameter search for the best fit to the data, a value of k_1 = 200 liter mole^{-1} sec^{-1} was settled on. This is considerably larger than the ozone-TCE rate constant without UV of about 17 liter mole^{-1} sec^{-1}. But much less than the reaction rate of TCE with hydroxyl radical of > 10^6 liter mole^{-1} sec^{-1}! This may indicate that the rate of production of hydroxyl radicals from ozone is actually the controlling reaction.

Table 3: EXPERIMENTAL SPECIFIC OZONE UTILIZATION RATES.

Water type	Ozone utilization rate, w: (1/s)
Distilled water	0.000242
Distilled water with 10 ppm TCE	0.000723
Tap Water	0.000605
Actual groundwater sample	0.001710

SECTION V

EXPERIMENTAL SETUP

The behavior of a packed column as an ozonation reactor using both a bench- and pilot-plant-scale reactor system has been studied.

Bench-scale experiments have been conducted using a 100 mm inner diameter glass column of 940 mm height. The packing consisted of 10 mm glass Raschig rings with a packing height of 720 mm. Figure 3 shows a flow sheet of the experimental setup. As an ozone source a Welsbach T-816 ozone generator supplied with oxygen feed has been used.
Contaminated liquid is pumped out of the 200 liter feed tank and circulated through a constant temperature heat exchanger. A split flow is fed to the column through a regulating valve and a rotameter. Before entering the column the feed temperature is measured. After entering at the top of the column the feed is evenly distributed with a gravity distributor. After trickling down the packing the effluent is collected and passed out of the column through a valve. A split flow of the effluent is pumped through a UV spectrophotometer to measure the dissolved ozone concentration. Another split flow is used to take the GC samples for liquid phase TCE concentration measurement, and for chloride ion measurements.

An ozone - air mixture from the ozone generator is fed to the gas purge tube in the bottom of the column. The gas purger tube is used to ensure an even gas distribution. After rising to the top of the column through the packing , the exhaust gas stream is passed through a UV spectrophotometer to measure the gas phase ozone concentration, the TCE is measured via an on line quadrupole mass spectrometer..

For the pilot plant scale experiments a Plexiglass column of 300 mm inner diameter and 3350 mm height has been used. The packing consisted of 16 mm plastic Pall rings with a packing height of 2350 mm. To monitor the concentration profile along the packing seven evenly distributed sample ports have been installed. Figure 4 shows a flow sheet of the experimental setup. As a source of ozone a Welsbach ozone generator supplied with oxygen feed gas has been used. The prepared contaminated feed water is pumped out of the 3000 L feed tank and circulated through a recycle loop. A split flow from the recycle loop is passed through a flow meter and past a temperature measurement point to the top of the column where it is evenly distributed across the packing using a gravity distributor. While the contaminated liquid trickles down the Pall ring packing it passes the seven sample ports. At the bottom of the column a split flow of the effluent is pumped through a UV spectrophotometer to measure the dissolved ozone concentration. Another split flow is used to take GC samples for liquid phase TCE concentration measurement and samples for pH value and Cl⁻ ion concentration measurement. Ozone-oxygen mixture from the ozone generator is passed into the bottom of the column. Additional air from a compressed air line may be added to adjust the ozone concentration or the gas flow rate respectively. After rising through the packing a split flow of the exhaust gas stream is pumped through the UV spectrophotometer to determine the gas phase ozone concentration. A sample of this stream is fed through a capillary to the Quadrupole Gas analyzer to measure the partial pressure of TCE in the exhaust gas.
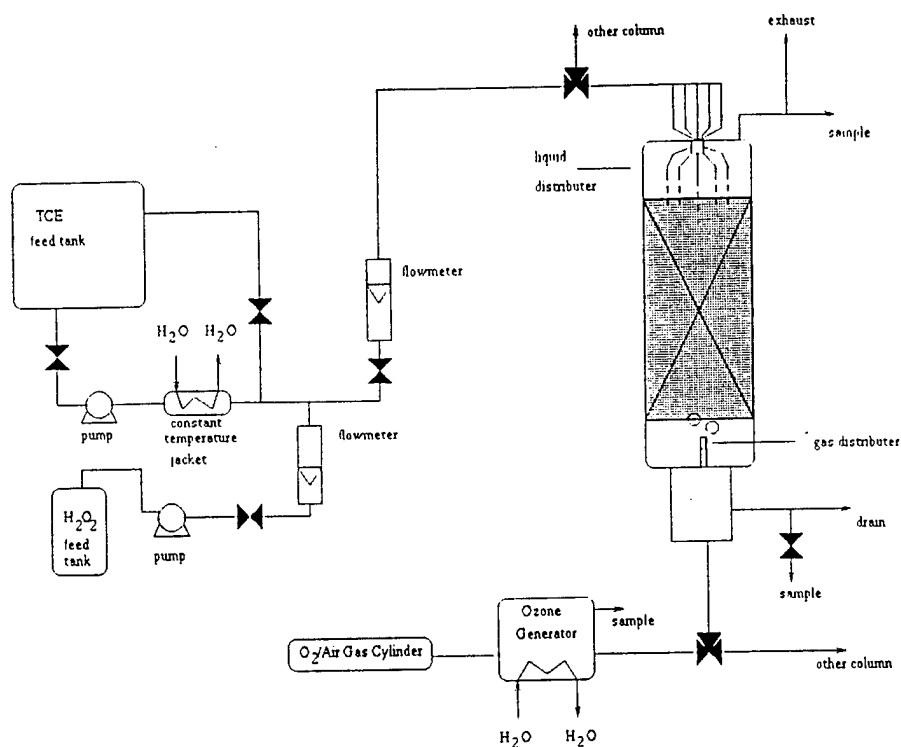
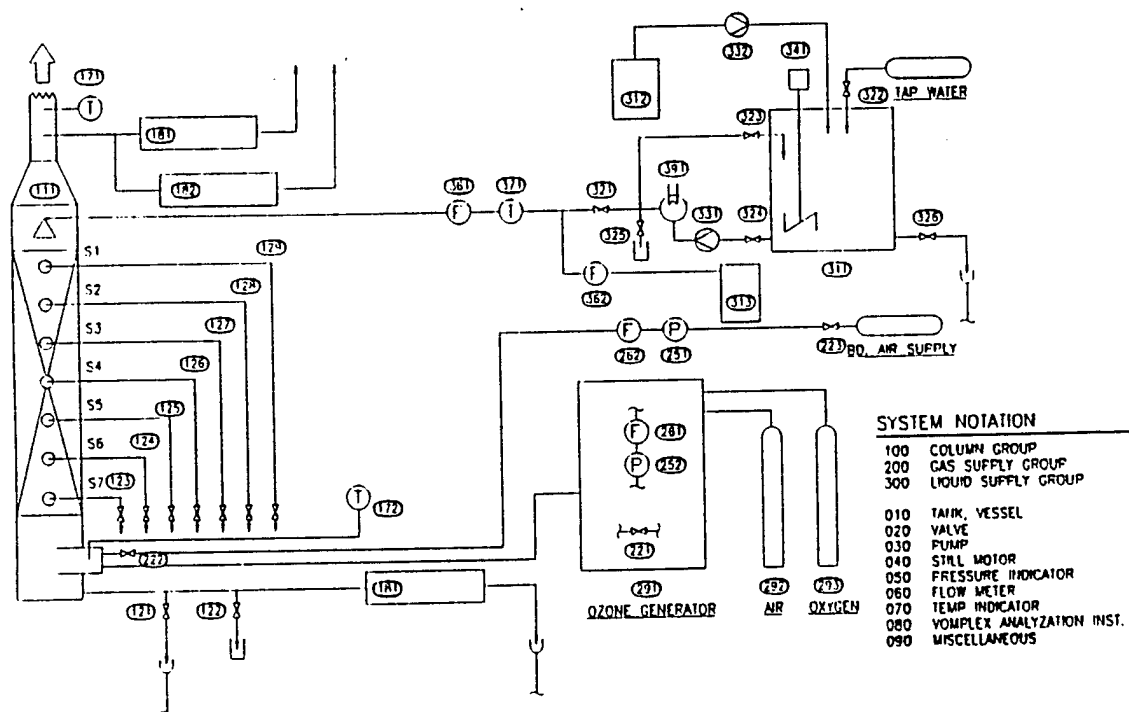Figure 3: Schematic of bench scale ozonation system.

SYSTEM NOTATION

100	COLUMN GROUP
200	GAS SUPPLY GROUP
300	LIQUID SUPPLY GROUP
010	TANK, VESSEL
020	VALVE
030	PUMP
040	STILL MOTOR
050	PRESSURE INDICATOR
060	FLOW METER
070	TEMP INDICATOR
080	VOMPLEX ANALYZATION INST.
090	MISCELLANEOUS

Figure 4: Schematic of pilot scale ozonation system.

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SECTION VI

ANALYTICAL

To monitor the behavior of the bench- and pilot-scale reactor, the ozone and TCE concentrations in both liquid and gas phase were measured. To measure the liquid-phase TCE concentrations gas chromatography was used. The gas chromatograph used was a HP 5890 Series II model equipped with an auto sampler and automatic injector. For separation a capillary column type DB 624 of 30 m length and 0.53 mm inner diameter was employed. Liquid samples of the feed, the effluent, and (in case of the pilot scale column) at the seven sample ports were taken in 2ml amber vials for postanalysis. Prior to sampling 60 µL of saturated sodium thiosulfate solution were added to each vial to terminate the reaction between ozone and contaminant at the time of sampling.

The pH value and chloride ion concentration of both feed and effluent water were measured using Orion pH and Cl⁻-ion electrodes. The chloride ion concentration was taken to be equal to the stoichiometric amount of TCE completely destroyed. To additionally ensure steady state at the time of sampling the temperature of the feed was measured using a bimetal dial thermometer.

Ozone concentrations of liquid phase effluent, feed gas and exhaust gas were measured using UV absorption of ozone. As a measurement instrument a Milton Roy spectronic 1001+ spectrophotometer equipped with two 50 mm pathlengh flow through cells was used. The measurement was done by feeding the appropriate stream through a flow cell (either gas or liquid) of the UV spectrophotometer and measuring the UV absorption.

Finally, the TCE concentration of the exhaust gas was measured using a Dycor quadrupole mass spectrometer. A sample stream was fed to the instrument which recorded the partial pressure reading for TCE in the gas stream.

SECTION VII

RESULTS

The removal and destruction of TCE were determined for both the bench scale and pilot scale columns over a range of G/L ratios, ozone concentrations, contacting patterns, and contact times. This range of parameters produces a wide variety of information on the removal efficiencies and destruction rates. Figures 5 and 6 show typical results for the bench scale ozone reactor experiments. The TCE removal and destruction as a function of ozone inlet concentration and volumetric gas to liquid ratio (G/L) in a countercurrent packed bed reactor are illustrated. One plot is for a fixed gas flowrate (400 ml/min), and the other for a fixed water flow (200 ml/min). The total removal is determined from GC measurements of the liquid phase, whereas, the TCE destruction is determined from chloride ion concentration measurements. The fairly large difference is assumed to be the amount of TCE volatilized or stripped from the solution. No partial oxidation products are seen. An interesting observation is that an apparent optimum in G/L ratio (~2) produces the greatest TCE destruction.
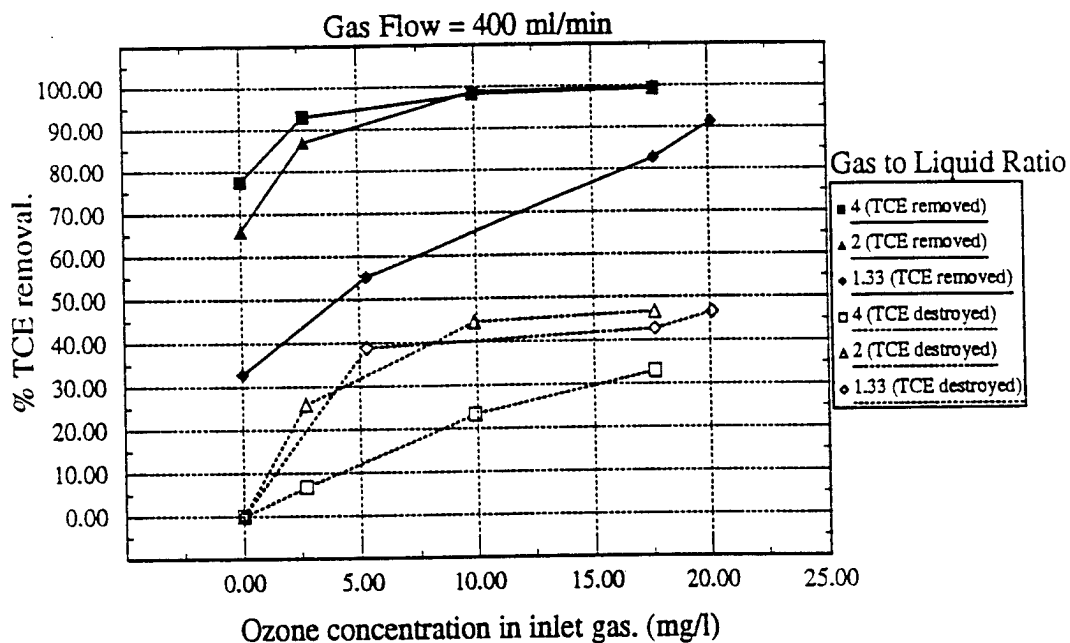

Figure 5: Effect of variations in inlet ozone concentrations at different G/L ratios on % TCE removal and destruction at constant vapor load.

Water flow = 200 ml/min

Gas to Liquid Ratio
- ■ 1 (TCE removed)
- ▲ 2 (TCE removed)
- ◆ 3 (TCE removed)
- ◻ 1 (TCE destroyed)
- ▲ 2 (TCE destroyed)
- ◇ 3 (TCE destroyed)

Y-axis: % TCE removal.
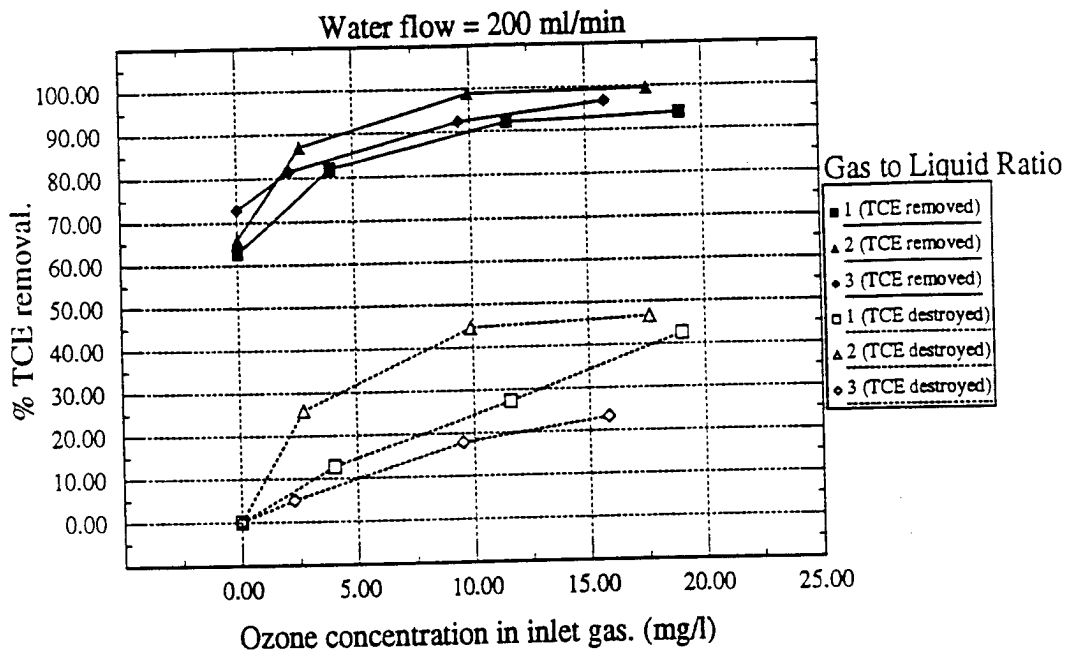X-axis: Ozone concentration in inlet gas. (mg/l)

Figure 6: Effect of variation in ozone feed concentrations at different G/L ratios on %TCE removal and destruction at constant liquid load.

The results of many such tests may be summarized by a plot of the fraction of TCE oxidized (FOTO) versus the G/L ratio as shown in Figure 7. This plot shows that in general, to minimize volatilization and maximized destruction on should employ low G/L ratio and high ozone feed concentration.
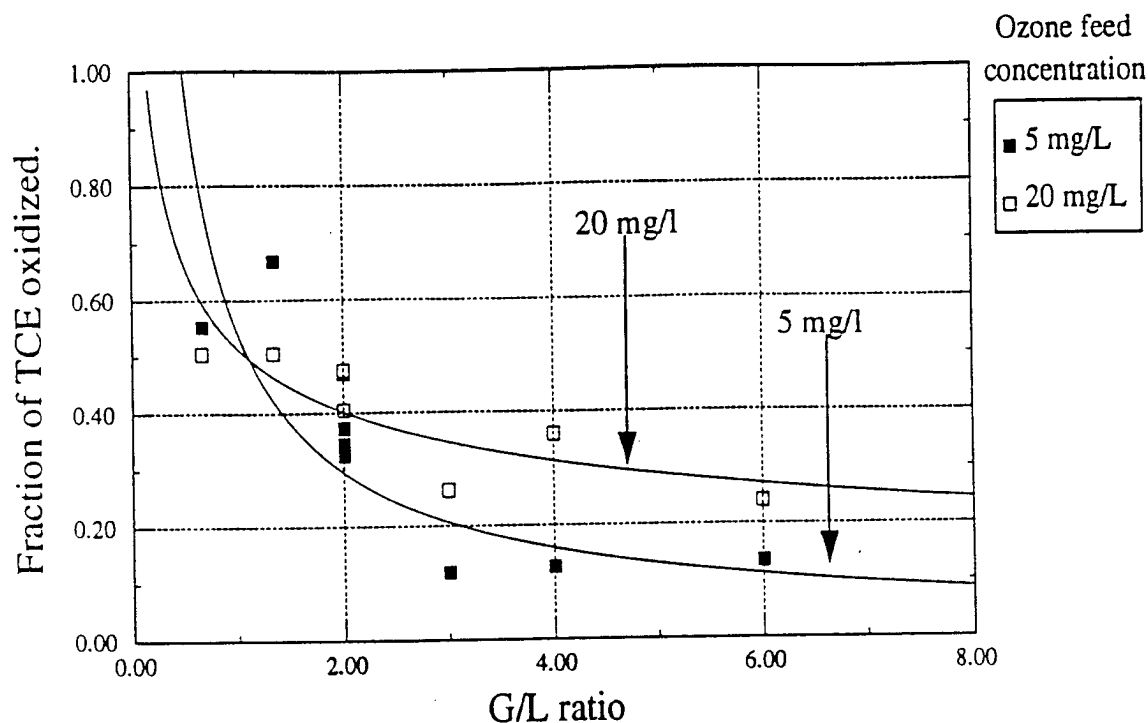
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Figure 7: Fraction of TCE oxidized (FOTO) as a function of G/L ratio.

Similar results for a cocurrent packed column indicate less volatilization and higher destruction, as might be predicted from the first order reaction model mentioned above.

The results for the pilot scale column operated in counter-current trickle bed mode, are essentially the same as for the bench scale column. However, in this case we may make a plot of the axial concentration of TCE and ozone in the column.

Figures 8, 9 and 10 show the axial concentration profile for liquid phase TCE concentration for different G/L ratios, Liquid loads, and ozone concentrations. Figure 8 illustrates the influence of G/L ratio on the effect of volatilization at a constant liquid flow of 12 l/min being equivalent to a liquid load of $2.9*10^{-03}$ m/s.
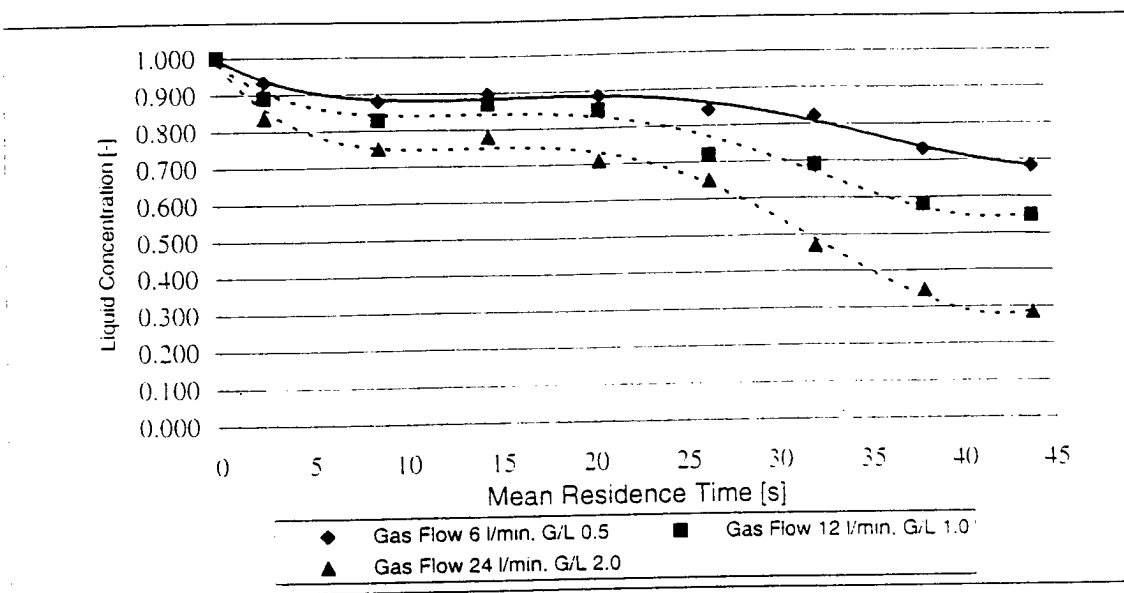
Figure 8: Influence of G/L ratio on Volatilization at 12 l/min water flow

As expected, the amount of TCE stripped increases from 30% at a G/L ratio of 0.5 to 72 % at a G/L ratio of 2.0. Figures 9 and 10 show the axial concentration profiles of liquid phase TCE concentration as a function of G/L ratio in a volatilization experiment at liquid flow rates of 12, 20, and 36 l/min.
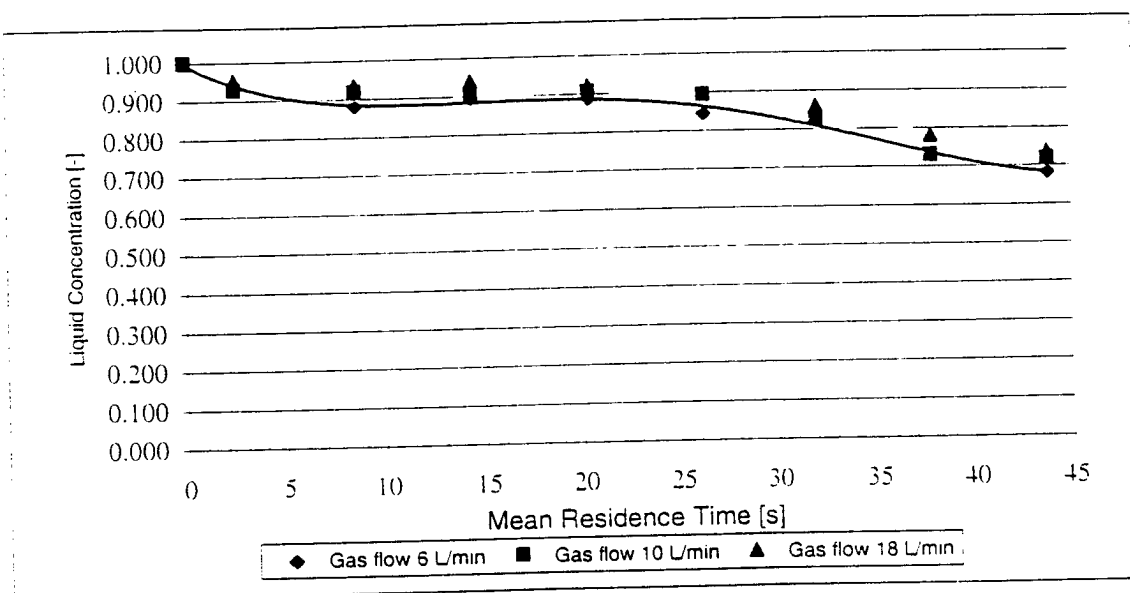

Figure 9: Liquid phase TCE concentration profiles at G/L ratio of 0.5

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As one might easily predict the amount of TCE being stripped increases with increasing G/L ratio. Figure 9 shows the concentration profiles for constant G/L ratio of 0.5 at liquid loads of $2.9*10^{-03}$ m/s, $4.8*10^{-03}$ m/s and $8.7*10^{-03}$ m/s. As shown in the figure, at this low G/L ratio, there is obviously no significant effect of liquid load on volatilization. The concentration profiles for the three liquid loads are almost identical. The total amount of TCE removed is about 30%. In comparison Figure 10 shows the same situation for a G/L ratio of 1.0.
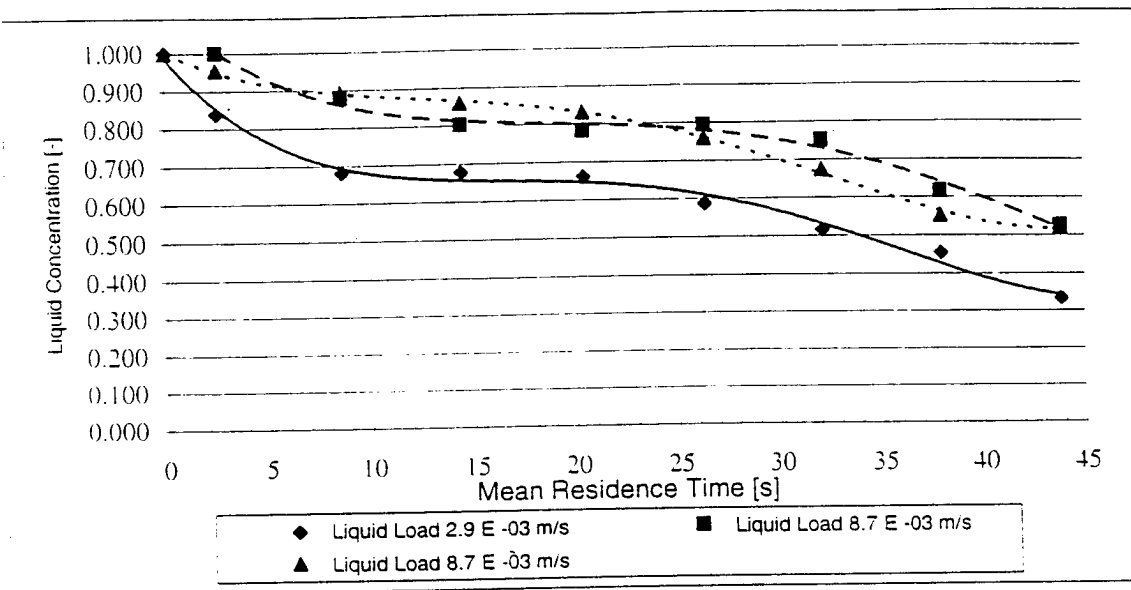

Figure 10: Effect of liquid load on Volatilization at G/L ratio of 1.0

For a Liquid load of $4.8*10^{-03}$ m/s and $8.7*10^{-03}$ m/s we see a total TCE removal of approximately 50%. When the liquid load is dropped to $2.9*10^{-03}$ m/s the amount of TCE stripped increases to about 70%.

Figures 11, 12 and 13 show the influence of ozone concentration on TCE removal at the above mentioned three different liquid loads at a constant G/L ratio of 0.5. As expected an increase in ozone feed gas concentration results in an increased TCE destruction.
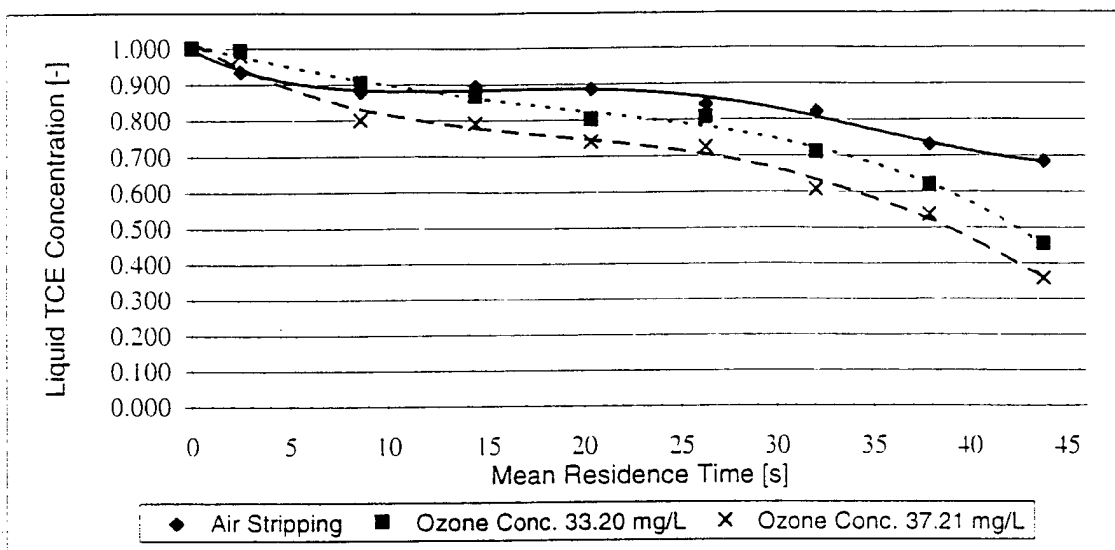
Figure 11: Concentration profiles at G/L ratio of 0.5, water flow 12 l/min

Figure 11 shows that an increase in ozone concentration of only 12% produces an increase in TCE destruction of 27 %. Figure 12 shows the same situation for a water flow of 20 l/min. Here as well a small increase in ozone concentration results in an almost doubled TCE destruction.
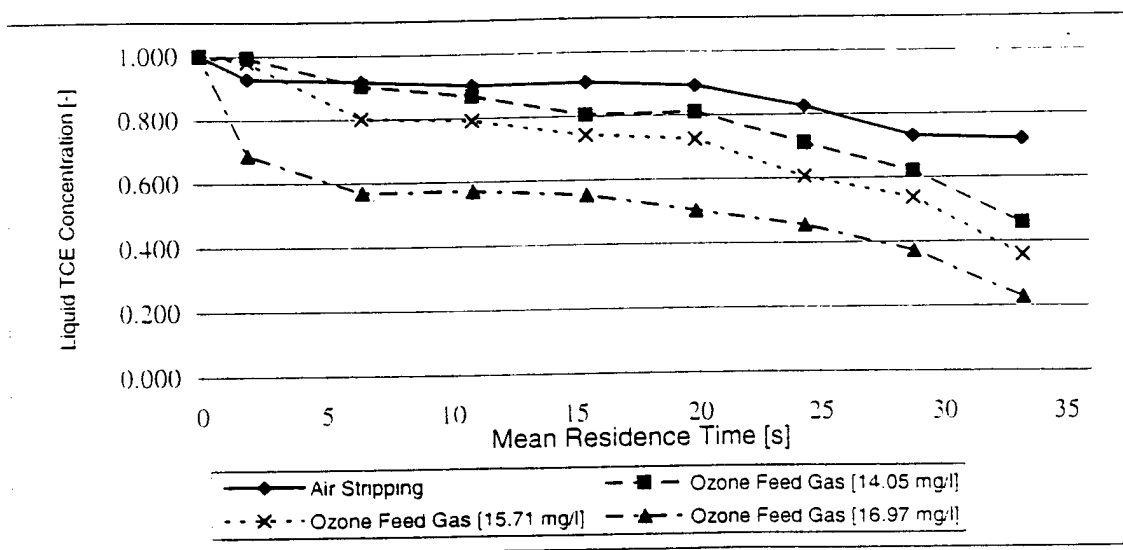

Figure 12: Concentration profiles at G/L ratio of 0.5, water flow 20 l/min.

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On the other hand Fig 13 indicates an optimal ozone concentration, because the increase in ozone feed gas concentration from 12.29 to 13.9 mg/l in this experiment does not result in an increased TCE destruction.
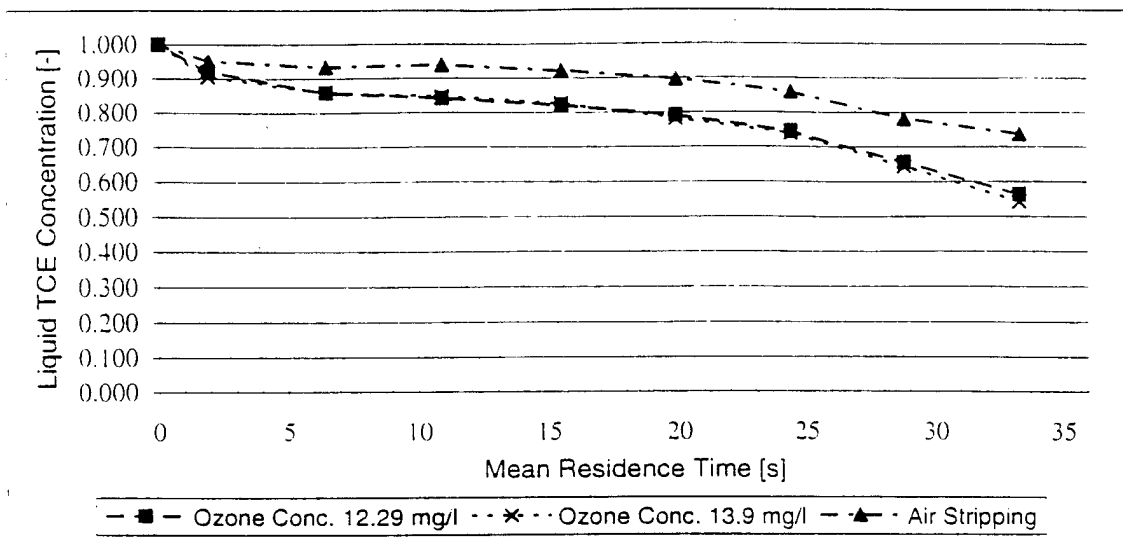

Figure 13: Concentration profiles at G/L ratio of 0.5, water flow 36 l/min.

Table 4 summarizes the data of an experiment done with a water sample from KI Sawyer AFB in the bench scale column.

TABLE 4: DATA OF EXPERIMENT WITH KI SAWYER AFB WATER SAMPLE

No.	G/L ratio	Gas flow	Water flow	Liquid load	Vapor load	TCE Conc. Feed	TCE Conc. Effluent	Ozone Conc. [mg/l]		TCE removed
	[-]	[l/min]	[l/min]	[m/s]	[m/s]	[ppm]	[ppm]	Feed	Off Gas	[%]
1	1.33	2	1.5	3.16e-03	4.22e-03	0.31	0.15	0	0	51.6
2	1.33	2	1.5	3.16e-03	4.22e-03	0.31	0.09	31.8	19.9	70.9
3 UV	1.33	2	1.5	3.16e-03	4.22e-03	0.31	0.07	31.8	18.5	77.4
4	2.00	3	1.5	3.16e-03	6.33e-03	0.31	0.09	27.8	2.9	70.9
5 UV	2.00	3	1.5	3.16e-03	6.33e-03	0.31	0.07	27.8	4.2	77.4
6	2.00	3	1.5	3.16e-03	6.33e-03	0.31	0.15	0	0	51.6
7	2.00	3	1.5	3.16e-03	6.33e-03	0.31	0.09	31.8	19.9	70.9
8 UV	2.00	3	1.5	3.16e-03	6.33e-03	0.31	0.07	31.9	18.4	77.4

Experiments were conducted at G/L ratios of 1.33 and 2 using a liquid load of $3.16*10^{-03}$ m/s. For the G/L ratio of 1.33 trials were done for a ozone feed gas concentration of 31.8 mg/l with and without UV light. At the G/L ratio of 2.0 ozone concentrations of 27.8 mg/l and 31.8 mg/l each with and without UV light were used.

At the given conditions, the effect of air stripping at both G/L ratios is about 51%. With the use of ozone at either concentration the amount of TCE removed increases to ca. 70%. This means that approximately 20 % of the feed TCE are destroyed in the reaction. The fact that a change in ozone feed gas concentration has no effect on the amount of TCE removed indicates that the concentration of 27.8 mg/l is already close to the optimal ozone concentration. To increase the amount of TCE reacting it is necessary to raise the concentration level of OH radicals. This is achieved by using UV light. The result is an increase of TCE destruction to 27 %. All experiments done using UV light show an increase in the amount of TCE reacted of about 7 % over the comparable experiment without UV light.

Table 5 shows the results of experiments done in the bench scale column to determine the effect of hydrogen peroxide on the system.

TABLE 5: BENCH SCALE COLUMN EXPERIMENTS, EFFECT OF HYDROGEN PEROXIDE

No.	G/L	G [l/min]	L [l/min]	Liquid Load [m/s]	TCE removed [%]	Ozone conc. [mg/l]	H_2O_2 ratio
1	0.5	0.2	0.4	8.44e-04	16	0	0
2	0.5	0.2	0.4	8.44e-04	36	12.66	0
3	0.5	0.2	0.4	8.44e-04	61	12.66	4
4	0.5	0.2	0.4	8.44e-04	62	12.66	4
5	0.5	0.2	0.4	8.44e-04	48	12.66	5
6	0.5	0.2	0.4	8.44e-04	55	12.66	6
7	0.8	0.4	0.5	1.05e-03	29	13.41	0
8	0.8	0.4	0.5	1.05e-03	43	13.41	0
9	0.8	0.4	0.5	1.05e-03	55	13.41	4
10	0.8	0.4	0.5	1.05e-03	67	13.41	5
11	0.8	0.4	0.5	1.05e-03	70	13.41	6

TABLE 6: BENCH SCALE COLUMN , EFFECT OF UV LIGHT

No.	G/L	G [l/min]	L [l/min]	Liquid Load [m/s]	TCE removed [%]	Ozone conc. [mg/l]	UV light
1	0.4	0.2	0.5	1.05e-03	12.9	0	off
2	0.4	0.2	0.5	1.05e-03	39.1	12.66	off
3	0.4	0.2	0.5	1.05e-03	53.9	12.66	on
4	0.66	0.4	0.6	1.26e-03	22.8	0	off
5	0.66	0.4	0.6	1.26e-03	29.0	13.41	off
6	0.66	0.4	0.6	1.26e-03	38.7	13.41	on
7	0.66	0.4	0.6	1.26e-03	59.3	19.09	off
8	0.66	0.4	0.6	1.26e-03	91.3	19.09	on

Figure 14 shows an example of typical error bars of a TCE concentration profile measurement. Because of the rapid concentration change at the top of the column, the error for these concentration measurements are significantly higher than those of measurements at the bottom of the column.
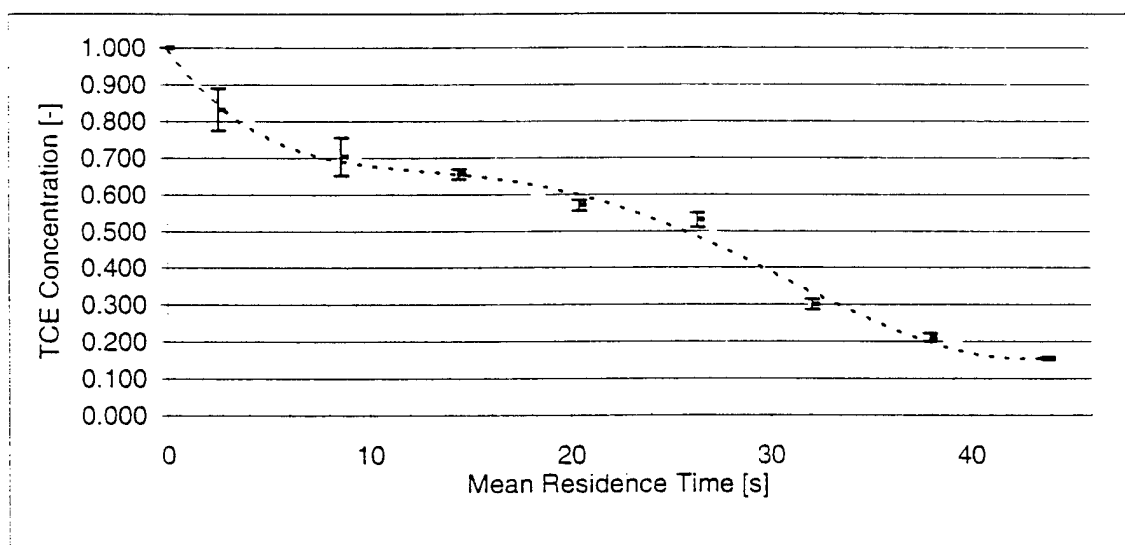

Figure 14: Typical measurement errors for concentration profiles

Figure 16 also shows the effect of G/L ratio for a gas stream with similar ozone concentrations (9 to 12 mg/liter). Note that the total removal approximately doubles over the volatilization alone at the same G/L ratio. Here the maximum removal occurs at a G/L ratio of 1, thus providing the greatest difference between volatilization and destruction. Finally, figure 17 shows the effect of inlet ozone concentration on TCE removal at a fixed G/L ratio of 0.5. Notice the large difference in TCE removal for relatively small increases in ozone concentration. Going from 30% removal with zero ozone to nearly 80% removal for ~17 mg/liter.

There is an apparent optimum in G/L ratio for a given ozone concentration; but with the range of variable being considered, a model is needed to understand the tradeoffs in finding the best reactor configuration, and understand the interaction between variables.

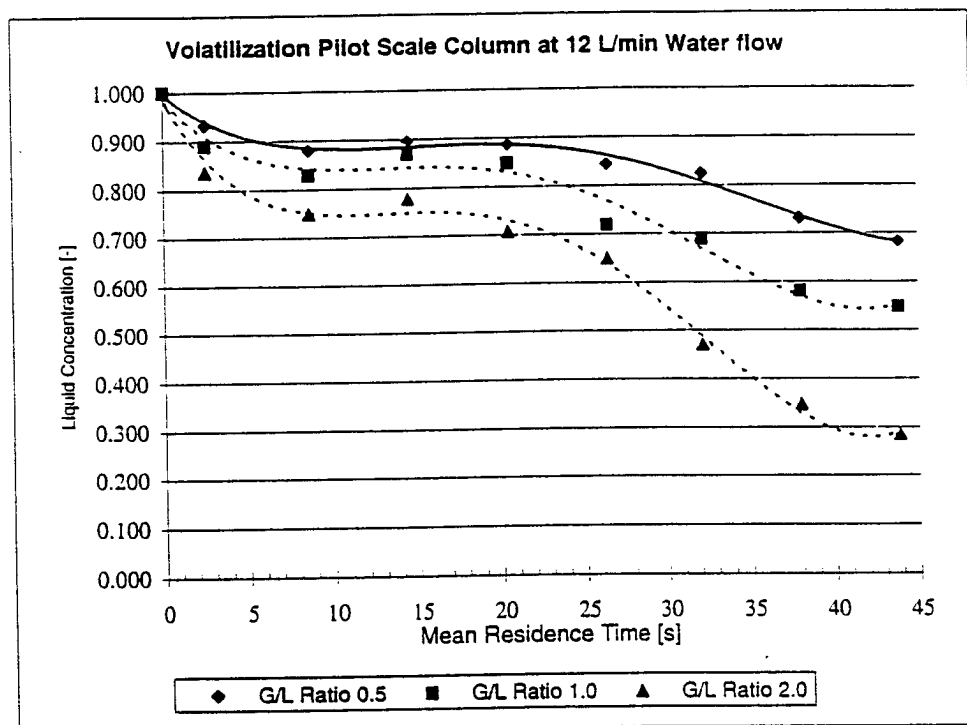**Volatilization Pilot Scale Column at 12 L/min Water flow**

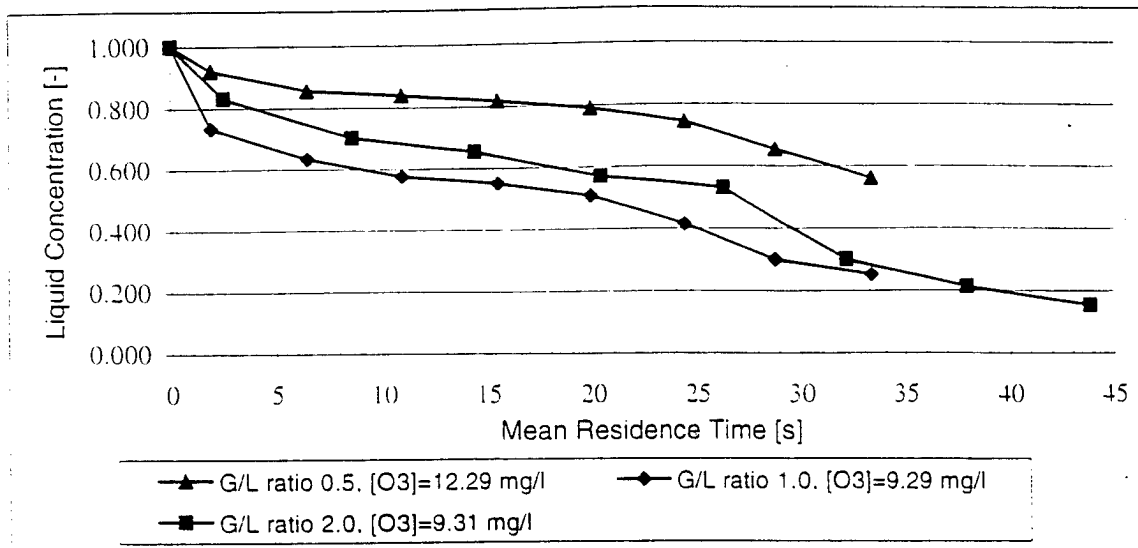Figure 15: The effect of G/L ratio on volatilization of TCE.

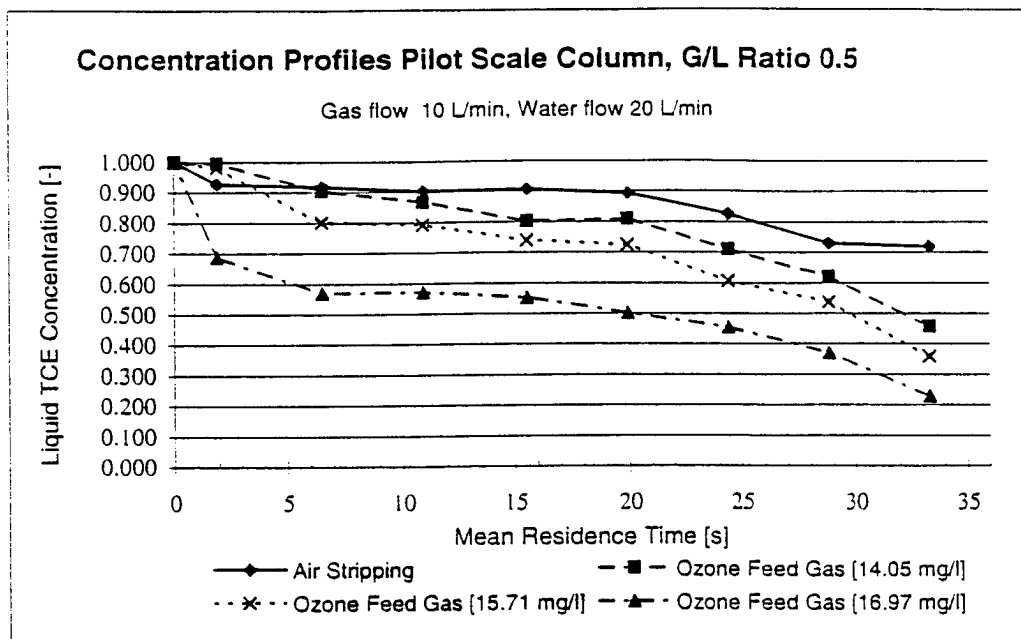Figure 16: The effect of G/L ratio for a fixed ozone concentration on TCE removal.

Figure 17: Effect of ozone concentration on TCE removal at a fixed G/L ratio.

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SECTION VIII

PACKED COLUMN REACTOR MODEL RESULTS

The four mass balance equations have been solved to produce the axial concentrations profiles of TCE and ozone in both the water and gas phase as a function of residence time, t, for the cocurrent reactor case, and matched to fit the experimental results within 5%. The results are shown in the attached Figures 18 and 19 - one for TCE and the other for ozone. There are several things to note about these plots. First, in the TCE plot the TCE concentration falls about 90% in the first minute and then levels out quickly. Therefore, it seems that residence times of greater than 1 minute don't significantly increase destruction. The gas phase TCE is basically the amount stripped by the gas. This passes through a maximum at about 20 second residence time, and then decreases and levels out at less than 3% of the initial TCE value. This indicates that for low gas/liquid ratios less than 3% of the TCE is stripped in the cocurrent mode, far less than in the counter current case. This low rate of stripping is promising, but the TCE destruction leveling off at about 90% may not be adequate for some environmental cleanup situations.

The ozone plot shows that 90% of the gas phase ozone is gone within 40 seconds of contact time, and the liquid phase concentration never rises very high (although this is still much greater than the TCE concentration). Due to decomposition, the overall rate of ozone disappearance is somewhat greater than that for TCE. That is why the TCE destruction levels off - there is very little ozone left to react. The ozone concentration in the water is quite low because the ozone is reacting almost as fast as it can be transferred to the water. This indicates the overall reaction may be slightly ozone mass transfer limited, but the specific rate of ozone utilization may be a bigger problem.

The bottom line is how these results may affect the design of the reactor. For TCE it appears that each reactor stage should not have a contact time of more than 1 or 2 minutes, whereas a holdup time for the gas phase of no more than 30-40 seconds is
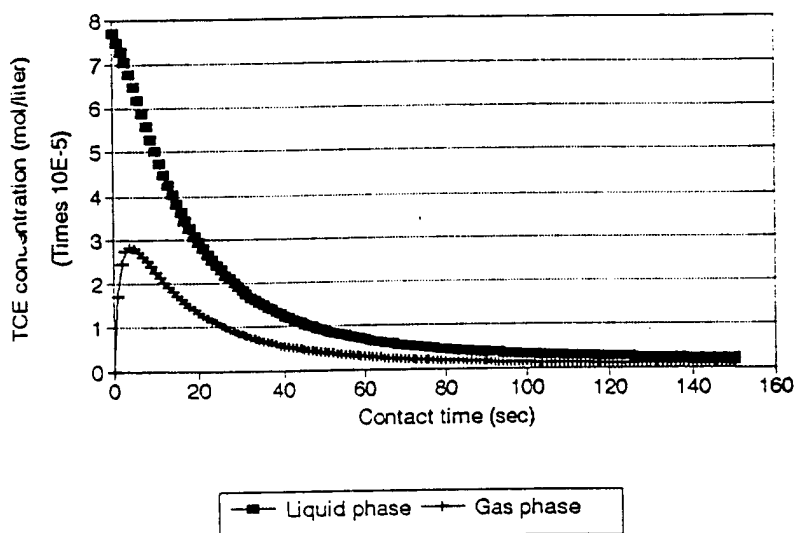

Figure 18: Cocurrent plug flow model predictions for TCE concentration as a function of contact time.
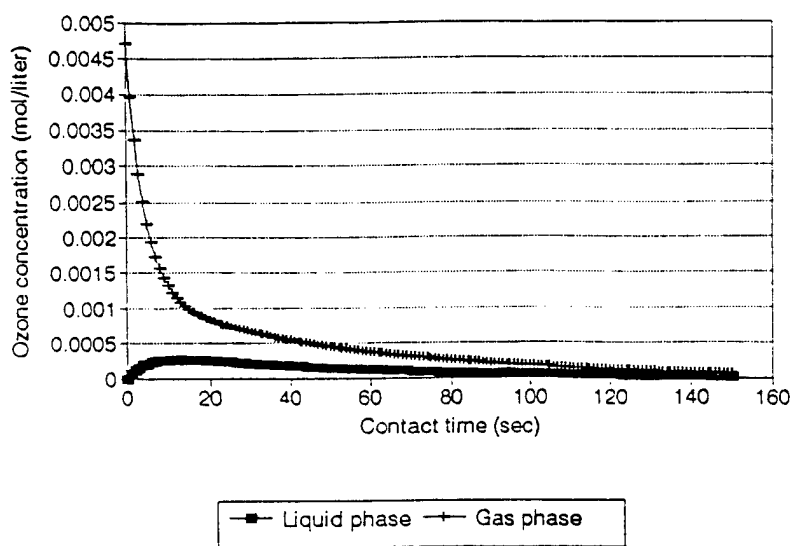
Figure 19: Cocurrent plug flow model predictions for ozone concentration as a function of contact time.

adequate. With a low volumetric gas flowrate, TCE stripping should not be too much of a problem and could be handled by a carbon bed, although there may be enough reaction (even though it is small) in the gas phase to destroy the TCE amounts involved. (We neglect this in the current model.) A major factor in the reactor design is the model observation that the TCE destruction levels out at around 90% to 95% as the ozone is depleted. This will clearly not be acceptable if high removal rates (>99%) are required by environmental regulations. There are two ways to solve this problem. One is to go with a large excess dosage of ozone. However, due to the high cost of producing the ozone, this solution may be prohibitively expensive. Another solution would be to use a two stage reactor with the water flowing through them in series, and fresh ozone feed evenly divided between the two reactors in a parallel fashion. Of course, adding additional reactors in series with parallel ozone feeds would probably improve the operation somewhat, but each additional reactor has a decreasing improvement. Another possibility is to add ozone at several points up and down one column. This would have the same general effect as splitting up the column into several parts.

Finally, the model tends to point towards the use of rather stocky columns with a length to diameter ratio (L/D) of somewhere between 6 to 10. Unfortunately, this type of design does not lend itself to ideal reactor analysis as well as larger L/D ratios (> 12) which more closely approach ideal PFR behavior. In a broad sense, the length to diameter of the column might affect these model results. A column too short and broad might deviate significantly from ideal plug flow, one of our basic model assumptions, and adversely affect reactor performance. Dye tracer studies can be used to determine how close to ideal performance the reactor is actually operating, and any deviation could be accounted for. Unfortunately, the model to take nonideal performance into account involves second-order differential terms and split boundary conditions, and takes a considerable time to implement.

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In terms of the reactor operation, the model also has several implications. In principal, all that needs to be determined for the water to be treated is w, and with that information the model should allow prediction of the necessary ozone dosage, contact time, and flowrates for the groundwater to be treated. Each different water source will have its own particular specific ozone utilization rate, w. This is especially true for "real" groundwater where alkalinity, pH, natural organic matter (NOM), metal species (Fe, Mg, etc.), dissolved gases (H_2S), and other factors can alter the ozone consumption (see Table III). We have noted that for the MTU reactor that iron oxides are precipitated onto the packing even from tap water. These factors make the water pretreatment steps (pH control, filtration, etc.) crucial in the successful application of ozonation technology. The main utility of reactor modelling will always be in defining the operational limits and range of performance of an individual piece of equipment within acceptable engineering limits.

SECTION IX

CONCLUSIONS AND RECOMMENDATIONS

A bench- and pilot-scale packed-bubble column ozonation reactor has been developed and tested for a variety of flowrates, ozone concentrations, and contacting patterns. A plug flow model has been developed for the cocurrent flow case. The adjustable parameters for this model have been determined from literature sources and from fitting to the results of experimental data. The model in turn was then used to study several design options and operating conditions. Some of the major findings of this study include:

♦ A packed-bubble column (PBC) is at least an order of magnitude smaller than a comparable open-bubble column.

♦ A countercurrent flow pattern demonstrated a high degree of TCE stripping, and relatively low oxidation. A cocurrent upflow column demonstrated the lowest volatilization and highest oxidation of TCE. The contacting pattern selected depends on the relative volatility and reactivity of the contaminants.

♦ To minimize TCE volatilization and optimize TCE oxidation, low G/L ratios and high ozone concentrations should be employed.

♦ For the reaction with TCE in pure water, a reactor contact time of approximately 2 minute for the water, and 1 minute for the ozone approaches the greatest destruction for the minimum volume.

♦ By determining the specific ozone utilization rate, w, for "real" groundwaters, the model may then be used to determine the appropriate reactor contact times to obtain a given degree of destruction. (By varying flow rates, or ozone dosage.)

♦ The models predict that the most efficient way of achieving high TCE destruction is to run the water phase through at least two reactors in series, and divide the ozone between the reactors in parallel.

♦ Actual groundwater may require high ozone dosages to achieve a high conversion. Proper water pretreatment is essential for efficient reactor operation.

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